Senior Thesis

Expansive Alkali-Silica Reactions In Concrete

by

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1987

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INTRODUCTION

"Alkali-silica reaction" is the term used to describe the chemical reaction that involves alkali cations and hydroxyl ions from concrete pore solutions and certain siliceous aggregates occasionally used in concrete. This reaction will occur only under specific conditions. The reaction product is an alkali-silica gel which is capable of water uptake. This causes expansion and cracking and, in some cases, leads to the complete destruction of the concrete. These reactions were first discovered by Thomas E. Stanton in 1940 (Hobbs, 1978). The current concern of alkali-silica reaction is due to two major factors; (1) an increase towards higher alkali contents of cement, and (2) the use of marginal aggregates with unknown service records (Diamond, 1975). This paper will discuss the different reactive aggregates, the conditions in which alkali-silica reactions occur, and the mechanism of alkali-silica reactions.

Reactive Silica Aggregates

Silica occurs in a variety of crystal forms which have varying degrees of reactivity with hydroxyl ions. The amount of gel produced and the rate of the reaction both depend on the type of silica aggregate. Deleterious effects caused by the expansive reactions may occur within a year as with opal or may take up to 20 years, as sometimes found with quartz.

Opal

Opal ($SiO_2 \cdot nH_2O$), which is the hydrous form of silica, is considered to be the most alkali reactive mineral. It is metastable, has an amorphous structure, and has a high water content (between 4 and 9 percent by mass). The structure consists of an extensive system of interconnected pores throughout the material. These components all contribute to the high susceptibility of hydroxyl ion attack.

Opal may occur as a constituent of cherts, flints, shales, sandstones, carbonate rocks, and volcanic rocks.

Tridymite and Cristobalite

Tridymite and cristobalite are crystallographically well defined forms of silica. Both minerals are metastable under normal conditions and are characterized by a very open structure through which hydroxyl ions can very easily penetrate. Both are highly reactive but are not usually found in well crystallized form in concrete aggregates. Although, poorly crystalline material of this nature (usually described as opal) occurs frequently and is often found in concrete aggregates.

Chalcedony

Chalcedony is a crypto-crystalline variety of silica with a very complex structure. A microscopic view of chalcedony shows it to be composed of radiating sheaf-like bundles of fibers embedded in a non-fibrous silica. Chalcedony has a spongy pore structure which contains interconnected spherical pores and larger voids that are similar to those in opals (Dolar-Mantuani, 1983). The expansion of chalcedony is relatively slow compared to the metastable silica minerals. Chalcedony occurs commonly in cherts, flints, agates, shales, phyllites, slates, and volcanic rocks.

Chert and Flint

Chert and flint are rock varieties which may consist of chalcedony, opal, crypto-crystalline quartz or any combination of these minerals. Chert usually occurs as nodules, lenses, or beds in sedimentary deposits but may sometimes form vast layers in a geologic sequence. Flint is a dark and hard variety of chert occurring especially in nodular form in chalk. Cherts and flints vary widely in their reactivity; some are very reactive, while others are not reactive at all. The variety that is most reactive are weathered cherts. These cherts are light-colored, have a chalky appearance, splintery fracture, and are more porous than other cherts.

Volcanic Glasses

Volcanic glasses either form rocks such as obsidian, perlite, pumice, and pitchstone or occur as ground mass of volcanic

rocks such as rhyolites, dacites, andesites, and basalts. Their microstructre is somewhat similar to opal, and they are unstable and very alkali reactive (Dolar-Mantuani, 1983).

The reactivity of volcanic glasses correlates to some extent with acidic character. Acidic glasses such as rhyolites, dacites, and andesites tend to be much more reactive than basalts. The reason for this being that acidic glasses are more siliceous (Diamond, 1976). The acidity of volcanic glasses is not the only determinant of its reactivity, as Kennerley, St. John, and Smith (1975) found when they compared the reactivity of obsidian and pitchstone (which had virtually identical compositions). The pitchstone was highly reactive while the obsidian was virtually inert. The differences between the two was the water content (3.5% for the pitchstone and only 0.14% for the obsidian). The reasons for the differences in reactivity are due to pores associated with the presence of water and a weakened internal structure due to interruption of silicon-oxygen linkages at sites of water molecules.

Quartz

Quartz is the thermodynamically stable form of silica, which is known for its resistance to chemical weathering. Although it is very stable, quartz too can be alkali reactive. Its reactivity is due to defects in the crystal lattice caused by metamorphic processes (Dolar-Mantuani, 1983). During metamorphism, the quartz grains become strained causing

deformation and disruption of the ordered crystal lattice structure, making the quartz less stable. Quartz is the least reactive form of silica and is very slow to expand.

Conditions For Expansive Alkali-Silica Reactions

There are several specific conditions that must be fulfilled before expansive alkali-silica reactions can occur. Of course, as already explained, the right type of aggregate must be present. Other conditions are, (1) the amount of reactive silica, (2) amount of alkali, (3) particle size of reactive silica, (4) climate, and (5) water-cement ratio.

Amount of Reactive Silica

The amount of reactive silica that causes both the maximum expansion and the maximum rate of expansion is known as the "Pessimum percentage" (Urhan, 1986). Expansion increases with increasing content of reactive silica until a maximum is reached and then decreases as the content of reactive silica is increased further (Mindess, Young, 1981). This is shown in Figure 1 (using opal as the aggregate).

When reactive particles are present in much larger or much smaller quantities than the pessimum, the expansion and damage will be smaller or no damage will occur. The pessimum percentage varies for the different forms of reactive silica. When the reactive silica content is below the pessimum, the amount of gel produced is insufficient to cause considerable

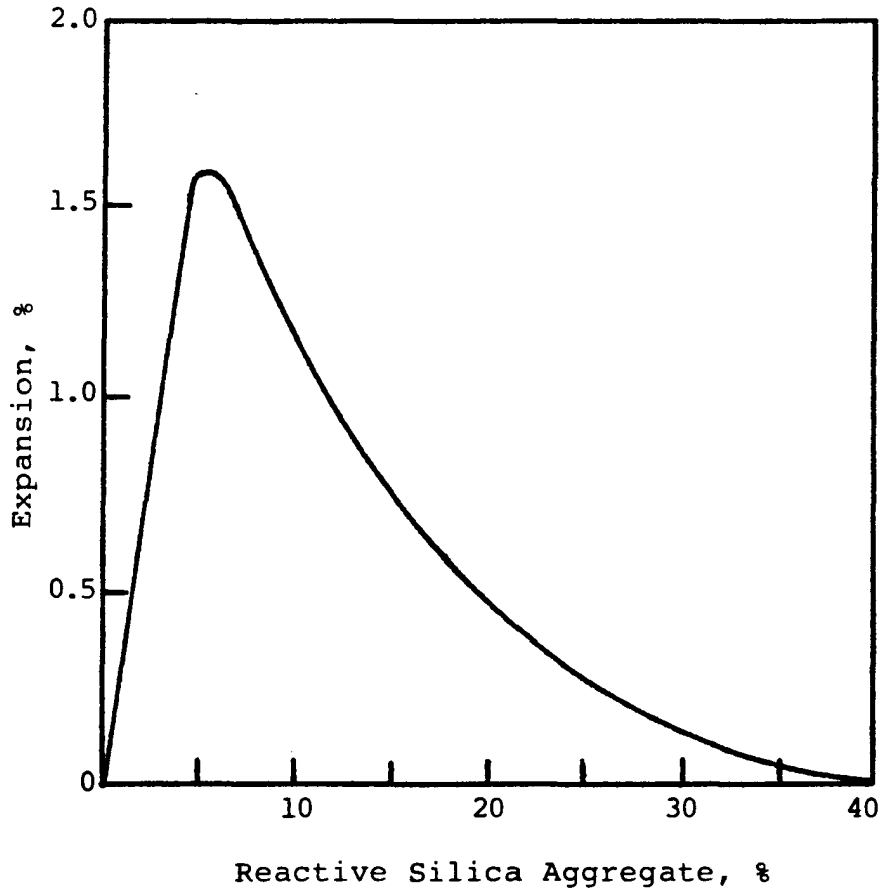

FIGURE 1. EFFECT OF THE CONTENT OF REACTIVE SILICA IN AN AGGREGATE ON THE EXPANSION OF CONCRETE DUE TO ALKALI-SILICA REACTION (From H. Woods, Durability of Concrete Construction, 1968)

damage. When the reactive silica content is far above the pessimum, there are not enough hydroxyl ions to sufficiently attack the large amount of silica. Thus, either no gel is formed or not enough is formed to cause damage to the concrete.

Amount of Alkali

The cement paste pores must contain solutions of sufficient alkali content. While most of the alkalies originate from the cement, others can be derived from external sources such as sea water, deicing salts, or different minerals high in soluble alkalies (Dolar-Montuani, 1983). The common alkalies that occur in cement are sodium and potassium. The combined amount of alkali present in cement is expressed as "percent Na_2O equivalent". This is calculated as $\%Na_2O + 0.66 \times \%K_2O$ (The factor 0.66 accounts for the difference in molecular weights of Na_2O and K_2O - Mindess, Young, 1981).

It has been found that the expansion of reactive aggregate is more closely correlated with the Na_2O equivalent than to the individual contents of sodium and potassium oxides (Hobbs, 1978). The amount of alkalies which causes expansion of concrete will vary with different reactive aggregates. Deleterious expansions will usually not occur below alkali concentrations of 0.6% Na_2O equivalent (See Figure 2 - (Dolar-Mantuani, 1983).

Particle Size of Reactive Silica

The particle size of the reactive material can also be an important factor. Highly reactive opaline particles are

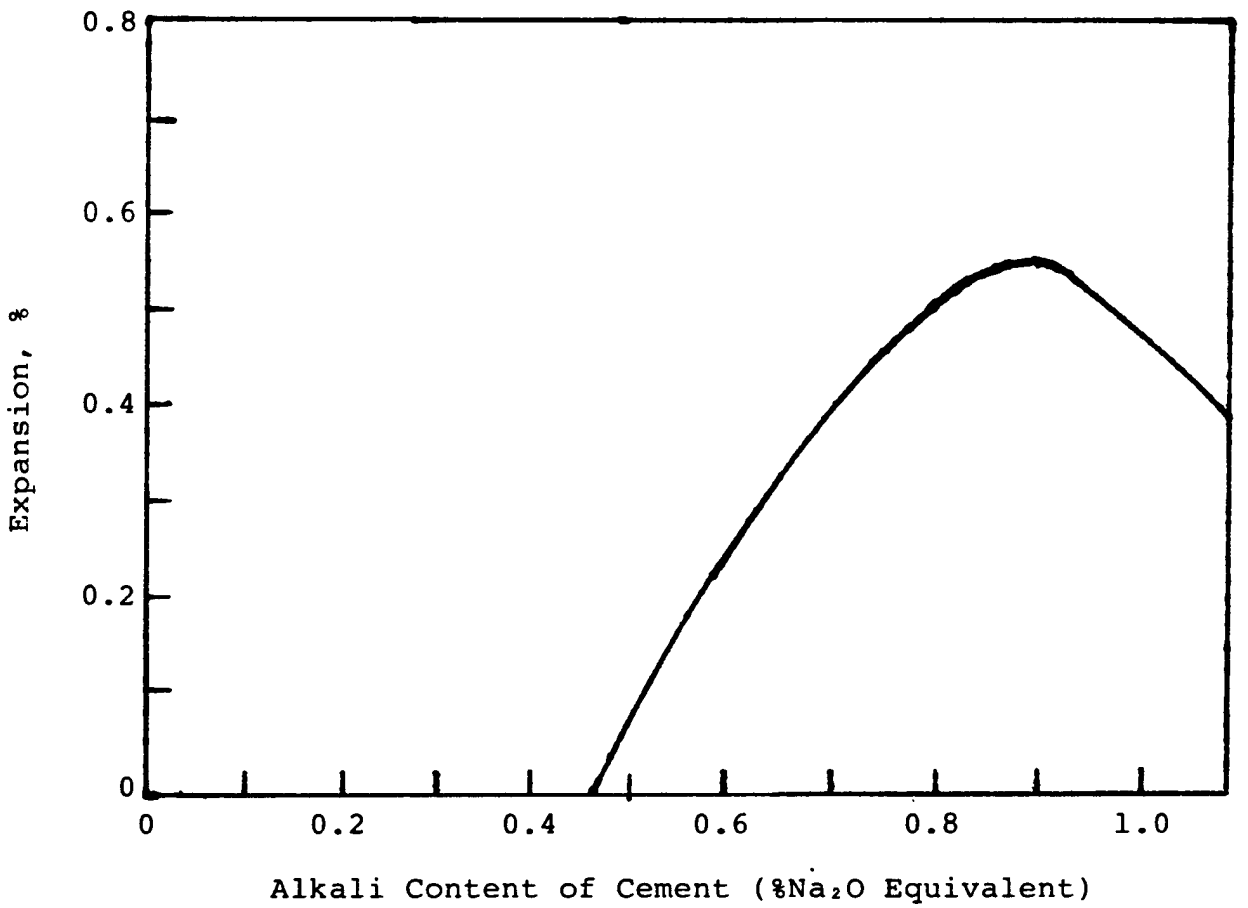

FIGURE 2. EFFECT OF THE ALKALI CONTENT OF THE CEMENT ON ALKALI-AGGREGATE EXPANSION (From H. Woods, Durability of Concrete Construction, 1968)

more expansively reactive in smaller sizes while the opposite is true for moderately reactive siliceous aggregates A particle size between 0.9 - 0.06 mm is found to provoke the maximum expansion by alkali silica reaction (See Figure 3 - Mindess, Young, 1981).

Climate

For alkali-silica reactions to occur the concrete must be exposed to moist or wet conditions. This is required since water must be present as pore solutions for an exchange of ions to occur between the aggregates and the solution. Water is also needed to cause the expansion of the gel formed during the reaction. Temperature also has an effect on expansive reactions. The rate of reaction is accelerated and the amount of expansion is increased as the temperature is increased (Gramlich, Verbeck, 1955). This is true because silica is more soluble at higher temperatures (Urhan,1987).

Water-Cement Ratio

The water-cement ratio refers to the amount of water used in the original mix design of the concrete. Low water-cement ratio reduces the expansion of concrete. This is the result of low permeability of the cement paste which retards the movement of water to the reaction products. Considerable expansion does not occur with water-cement ratios below 0.4 (see Figure 4 Gramlich, Verbeck,1955).

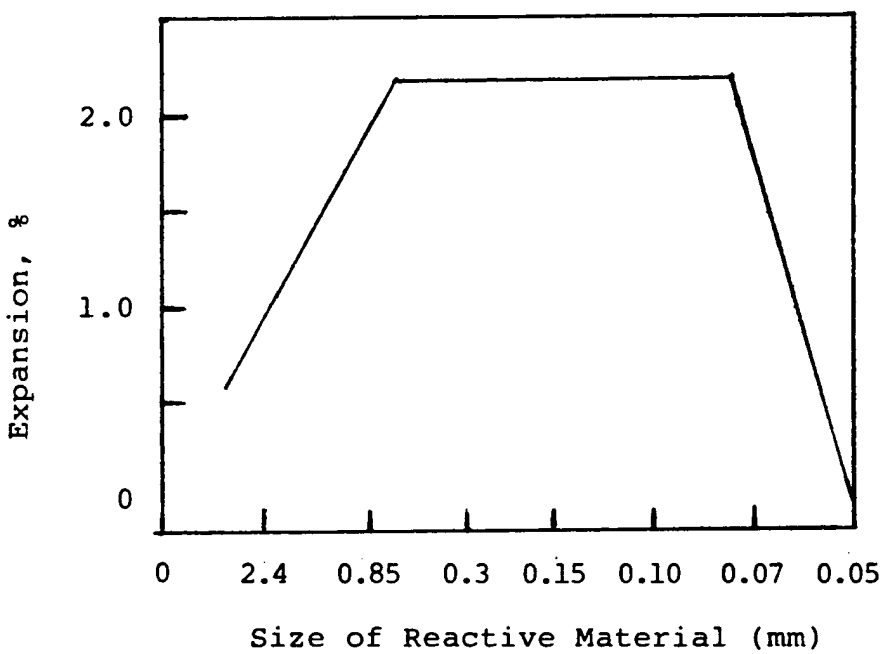

FIGURE 3. EFFECT OF THE SIZE OF REACTIVE SILICA CONSTITUENT OF AGGREGATE ON ALKALI-AGGREGATE EXPANSION (From H. Woods, Durability of Concrete Construction, 1968)

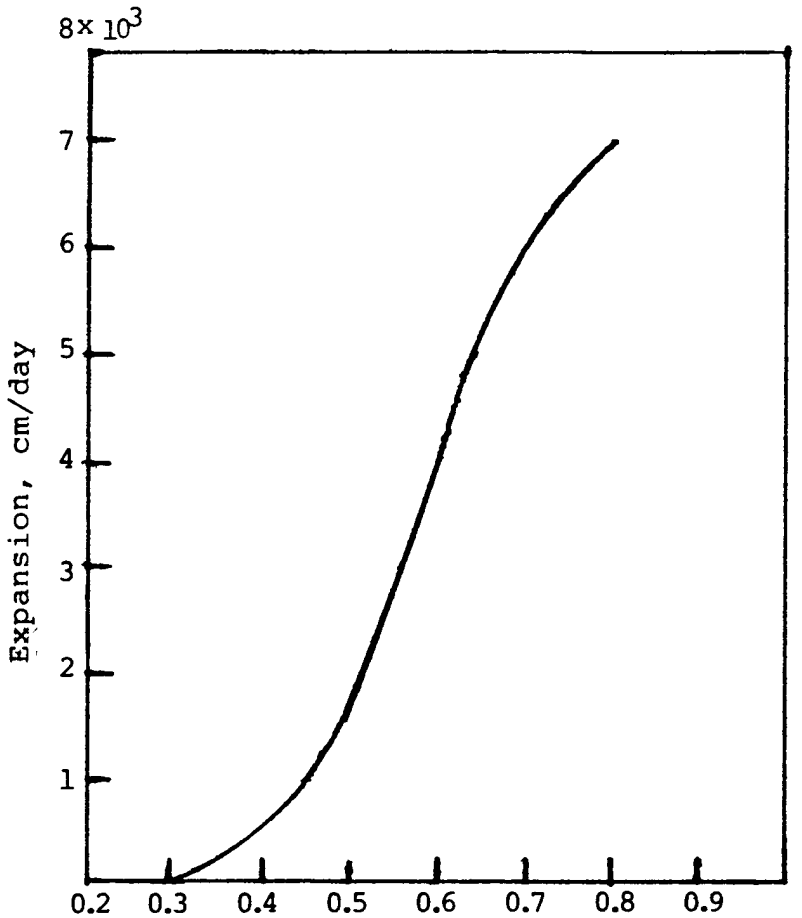

FIGURE 4. EFFECT OF WATER-CEMENT RATIO ON EXPANSION (From Gramlich and Verbeck, American Society for Testing Materials Vol. 55, 1985)

Mechanism of Alkali-Silica Reactions

The chemical reaction that causes distress in concrete involves an attack on susceptible aggregate grains by dissolved components of the pore fluid of the concrete. This chemical attack breaks down the reactive aggregate which reacts with the sodium and potassium hyroxides of the pore fluid to form an alkali-silica gel.

$$S + N(K)H \longrightarrow N(K)\text{-}S\text{-}H$$

aggregate pore fluid alkali silica gel

This gel has the ability to imbibe considerable amounts of water, which is accompanied by a volume expansion. If the expansion is suffcient it will crack the weakened aggregate and the surrounding cement paste (Mindess, Young 1981).

The actual chemical attack of the siliceous aggregate does not involve alkali ions, but rather, hydroxide ions. Alkali ions are released into the pore solutions from the cement during hydration. These alkali cations generate an equivalent amount of hydroxide ions into solution. Therefore, the hydroxide ions in solution will eventually equal the combined concentrations of the sodium and potassium cations (Diamond, 1975). As a result, the pH (the measurement of OH ion activity) of the pore solution of high alkali cements reaches the range of 13.5-13.9. Also, the OH^- concentration is about 0.7 M, more than fifteen times that of pure $CA(OH)_2$ solutions (Urhan, 1987). This elevated pH of high alkali cements is very important, since the dissolution of reactive

aggregate increases with increasing pH (See table below).

Table 1. Effect of pH on the Solubility of Amorphous Silica in a Cement Paste (From Mindess and Young, Concrete, 1981)

medium	pH	approximate solubility of SiO_2 (ppm)
Neutral water	7	100-150
Moderately alkaline water	10	500
Saturated $Ca(OH)_2$	12	90,000
Low-alkali cement paste	~12.5	500,000
High-alkali cement paste	>13.0	infinite

Attack of OH^- on Silica

Attack on well-crystallized or other relatively dense forms of silica takes place mainly at the surface of the aggregate. Poorly crystallized hydrous silica, on the other hand, permits penetration of hydroxyl and sodium (or potassium) ions into its interior (Glasser and Kataoka, 1981). The attack of the OH^- on the silicon atom increases its coordination number and weakens the oxygen-silica bonds. The silicon atom will then go into solution as a silicate ion: $Si(OH)_4$ Other silicate ions in addition to $Si(OH)_4$ will then be formed by addition of hydroxyl ions:

$$Si(OH)_4 + OH^- \rightleftharpoons Si(OH)_5^-$$

$$Si(OH)_5^- + OH^- \rightleftharpoons Si(OH)_6^{=}$$

These negatively charged silicate ions are electrically balanced by positive ions from the cement pore fluid. Since sodium and potassium are essentially the only cations present in the pore fluid of mature paste, the result is the formation of an alkali silicate gel. (Blanchard, Figg, Pettifer and Rayment, 1985). The over-all reaction can be

given as (Urhan, 1987):

$$SiO_2 + 2OH^- + 2Na^+(K^+) \longrightarrow Na^+(K^+)SiO_2 \cdot H_2O$$

As the reaction continues the concentrations of hydroxyl ions and alkalies will decrease. Eventually the concentrations will become too low to continue forming considerable amounts of gel.

Alkali-Silicate Gel

The exact chemical composition of the gel will depend on the concentration of sodium and potassium ions in the cement paste pore fluid (Blanchard et. al., 1985). The gel is usually transparent or opaque, and has an amorphous structure. When the alkali-silicate gel is originally formed it is in a solid or quasi-solid state. This is when the critical expansion upon water uptake occurs, causing cracking of the aggregate and cement paste due to mechanical pressure. With further absorption of water the gel will become a fluid sol which escapes into the surrounding cracks and voids (Mindess and Young, 1981). This fluid sol will sometimes reach the top of the concrete, and upon drying will appear as a white powder on the concrete's surface.

SUMMARY

The two main factors that determine the chances of expansive alkali-silica reactions occurring in concrete are, (1) the alkali content of the cement, and (2) the type of aggregate. For deleterious expansions to occur in concrete the alkali content of the cement must be above 0.6% Na_2O equivalent. The type of siliceous aggregates that cause expansive reactions are susceptible to hydroxyl ion attack. The reason for their susceptibility is their crystal structure; it is either disordered, amorphous, or in some way imperfect. Also, a system of interconnected pores throughout the aggregate facilitates the attack of hydroxyl ions. The most common reactive aggregates are: opal, tridymite and cristobalite, chalcedony, chert and flint, volcanic glass, and strained quartz.

Other factors that are conducive to expansive alkali-silica reactions are, (1) an aggregate particle size between 0.9 - 0.06 mm, (2) wet or moist conditions, (3) a relatively high temperature, (4) a water-cement ratio above 0.4.

The mechanism of alkali-silica reactions can be broken down into six basic steps:

(1) Hydration of the cement paste.

(2) Alkali cations released into the cement pore fluid.

(3) The alkali cations generate an equivalent amount of hydroxyl ions.

(4) Hydroxide ions attack the reactive silica aggregate and release silicate ions into pore fluid.

(5) The silicate ions are electronically balanced by alkali cations to produce an alkali-silicate gel.

(6) The alkali-silicate gel absorbs water, causing it to expand and crack the aggregate and surrounding cement paste. If the expansion is considerable, it will cause cracking throughout the concrete and can lead to the complete deterioration of the structure.

REFERENCES CITED

Blanchard, J., Figg, J., Pettifer, K. and Rayment, P. Observations on the Mechanism of Alkali-Silica Reactions in Concrete: Rhythmic Reactions. Cement and Concrete Research. Vol. 15, 1985. pp. 21-26.

Diamond, S. A Review of Alkali-Silica Reaction and Expansion Mechanisms. 2. Reactive Aggregates. Cement and Concrete Research. Vol. 6, No. 4, 1976. pp. 549-559.

Diamond, S. A Review of Alkali-Silica Reaction and Expansion Mechanisms. 1. Alkalies in Cements and in Concrete pore solutions. Cement and Concrete Research. Vol. 5, 1975. pp. 329-346.

Dolar-Mantuani, L. Handbook of Concrete Aggregates. Noyes Publications. Park Ridge, N.J. 1983. pp. 82-96.

Glasser, L.S. and Kataoka, N. The Chemistry of Alkali-Aggregate Reaction. Cement and Concrete Research. Vol. 11, 1981. pp. 1-9.

Gramlich, C. and Verbeck, G. Osmotic Studies and Hypothesis Concerning Alkali-Aggregate Reaction. Presented at the 58th annual meeting of the American Society for Testing Materials. 1955. pp. 1110-1123.

Hobbs, D.W. Expansion of Concrete Due to Alkali-Silica Reaction: an Explanation. Magazine of Concrete Research. Vol. 30, No.105, 1978. pp. 215-217.

Kennerly, R.A., St. John, D.A. and Smith, L.M. Symposium Alkali-Aggregate Reaction, Protective Measures. Reykjavic, Iceland. 1975. p. 35.

Mindess, S. and Young, J.F. Concrete. Prentice-Hall, Inc., Englewood Cliffs, N.J. 1981. pp. 140-146.

Urhan, S. Alkali-Silica and Pozzolanic Reactions in Concrete. Cement and Concrete Research. Vol. 17, No. 1, 1975. pp. 141-152.

Woods, H., Durability in Concrete Construction. Monograph No. 4. American Concrete Institute, Detroit, MI, 1968.